min., yielding a colorless precipitate (1.01 g., 0.0068 mole, 34%), m.p. 97–98.5°. After recrystallization from ether the sample melted at 99.5–100.5°, mixed m.p. 100.5–101.5° with a sample of *N*-methylacetanilide prepared[13] from Eastman Kodak Co. White Label *N*-methylaniline. The infrared spectra of the two samples in Nujol were identical. ν_{NH} none; $\nu_{C=O}$ 1672 cm.$^{-1}$ in Nujol.

Decarboxylation of 9-methylcarbazole-1-carboxylic acid (IV), 9-Methylcarbazole-1-carboxylic acid[5] (0.50 g., 0.00221 mole) was mixed thoroughly with powdered soda-lime (2.5 g.) and the mixture decarboxylated as described previously. The white sublimate (0.23 g., 0.00127 mole, 58%), m.p. 87.5–89.0°, did not depress the melting point of authentic 9-methylcarbazole,[6] and the infrared spectra in Nujol were identical. ν_{NH} none.

Decarboxylation of 9-methylcarbazole-1,8-dicarboxylic acid (V). 9-Methylcarbazole-1,8-dicarboxylic acid[5] (0.50 g., 0.00186 mole) was decarboxylated as described previously. The white sublimate (0.17 g., 0.00094 mole, 50%), m.p. 84–86°, did not depress the melting point of authentic 9-methylcarbazole[5] (it is interesting to note, however, that the mixed melting point of equal quantities of carbazole and 9-methylcarbazole is 83–87°) and the infrared spectra in Nujol were essentially identical, except for the presence of a medium weak NH or OH band at 3500 cm.$^{-1}$, suggesting contamination by a small amount of carbazole, the *N*-demethylation product.

School of Chemistry
University of Minnesota
Minneapolis 14, Minn.

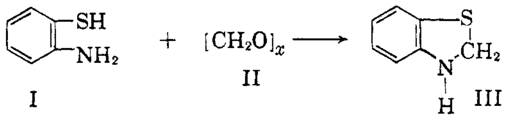
A New Synthesis of Benzothiazoline

Glenn L. Jenkins, Adelbert M. Knevel,
and Charles S. Davis

Received April 25, 1960

Although a number of syntheses for benzothiazoline have been reported in the literature,[1–4] none offers the convenience of the method which we report here.

We found that benzothiazoline (III) was formed in good yields by refluxing 2-aminobenzenethiol (I) with paraformaldehyde (II) followed by distillation under reduced pressure.



EXPERIMENTAL

To 12.5 g. (0.1 mole) of 2-aminobenzenethiol (American Cyanamid, tech. grade) dissolved in 20 ml. of anhydrous methyl alcohol was added a mixture of 4 g. of paraformaldehyde (Eastman Kodak, pract. grade) suspended in 10 ml. of anhydrous methyl alcohol. The mixture was refluxed until the original yellow color disappeared (about 12 hr.). Upon cooling to room temperature, two distinct layers formed. The bottom layer was withdrawn and distilled. The fraction collected at 146–149°/18 mm. was identified as benzothiazoline. The yield was 75–80% based on 2-aminobenzenethiol.

Identification of the product was accomplished as follows: (a) The infrared spectrum showed an intense nitrogen-hydrogen stretching band at 3.0 μ. (b) The boiling point was identical with that reported,[1,5] in the literature (b.p. 270°). (c) The phenylisocyanate derivative melted at 161–162°. The literature[5] value was 162°.

Acknowledgment. The authors are grateful to the American Cyanamid Co. for graciously supplying 2-aminobenzenethiol.

Research Laboratories
School of Pharmacy
Purdue University
Lafayette, Ind.

---

(1) M. Claaz, *Ber.*, **45**, 1031 (1912); **49**, 1141 (1916).

(2) M. T. Bogert and A. Stull, *J. Am. Chem. Soc.*, **47**, 3078 (1925).

(3) H. P. Lankelma and P. X. Sharnoff, *J. Am. Chem. Soc.*, **53**, 2654 (1931).

(4) K. Baker, *Helv. Chim. Acta*, **33**, 2011 (1950).

(5) R. A. Henry and W. M. Dehn, *J. Am. Chem. Soc.*, **71**, 2297 (1949).

Schiff Bases from 4-(4-Aminostyryl)quinoline and Aldose Sugars[1]

Carl Tabb Bahner, Norvell Hunt,
and Lydia M. Rives

Received May 2, 1960

4-(4-Aminostyryl)quinoline (I) reacted readily with 4-dimethylaminobenzaldehyde to form a Schiff base that was less toxic than I.[2] It seemed that aldose sugars might produce similar products and that the sugar moiety might cause the compounds to be water soluble. The use of a small amount of dimethylformamide made it possible to bring the reactants into a homogeneous liquid reaction mixture at the desired temperature, 120–130°. Glyceraldehyde, ribose, galactose(II), glucose(III), lactose, and maltose all seemed to react smoothly under these conditions, but only II formed crystals that were purified readily by recrystallization. The other products tended to precipitate as gels or amorphous solids.

EXPERIMENTAL

Galactose Schiff base of 4-(4-aminostyryl)quinoline. A mixture of 30.0 g. of I and 15.0 ml. of dimethylformamide was heated to 130° to produce a clear solution. This solution was cooled to 110°, 21.6 g. of II was added slowly with stirring, and the mixture was heated 10 min. at 120–130°. The resulting solid mass was washed with benzene and with water to remove excess starting materials. One gram of solid was dissolved in 30 ml. of dimethylformamide, 20 ml. of the solvent was removed by distillation at 60° at 2.5 mm. The bright yellow crystals which formed were recrystallized

---

(1) This research was supported by a grant from the National Cancer Institute.

(2) Carl T. Bahner, Clarence Cook, John Dale, John Fain, Fred Hannan, Patricia Smith, and Joan Wilson, *J. Org. Chem.*, **23**, 1060 (1958).